TOXICITY

to Greenhouse Roses from Paints Containing MERCURY FUNGICIDES

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Toxicity to Greenhouse Roses From Paints Containing Mercury Fungicides

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A NUMBER of greenhouse rose growers in the Northeast have recently experienced severe losses from mercury injury on Better Times, Briarcliff, and related roses of the Columbia strain (Butterfield, 1954). In each case the sash bars of the greenhouses had been coated with a white paint containing a mercury compound, added to protect the paint film against fungus attack. Such paints have contained as much as 0.84 per cent by weight of the fungicide di-(phenylmercuric) dodecenyl succinate (DPMDS)[2]. Apparently the fungicide is either volatilized directly or breaks down to metallic mercury, which vaporizes slowly from the paint film.

The symptoms of mercury injury on susceptible varieties of roses have been described by Zimmerman & Crocker (1934) and may be expressed in a number of ways. Flowers may be off-color, the petals ranging from bluish through pink to white or brown instead of the normal color. Young buds often fail to open and the bud scales turn brown. In such cases all the bud scales and petals can be lifted off the receptacle easily (see colored Figure 1, Zimmerman & Crocker, 1934). In addition to the above, chronic exposure of roses to mercury results in slow growth and reduced flower production. Leaves or flowers of peach, fern, calla lily, holly, camellia, tobacco, and many other plants are also injured by exposure to mercury vapor.

The present study was undertaken for a number of reasons. First, it was necessary to establish the toxicity of the paint to roses. Second, the nature of the volatile material responsible for injury was studied. Third, the effect of components commonly used in paints on the behavior of DPMDS was explored. Fourth, measurements were made to determine how long volatile mercury is liberated from a paint film, and fifth, treatments were sought which would reduce or eliminate the liberation of mercury from a paint film.

Materials and Methods

In certain studies standard paint samples were used. One, the standard control paint, was a white greenhouse paint that contained no mercury compound and contained titanium dioxide and zinc oxide as pigments. The standard mercury paint was identically formulated but contained 0.525 per cent DPMDS by weight.

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[1]Plant pathologist in charge and plant pathologist, respectively.

[2]In this paper di-(phenylmercuric) dodecenyl succinate is abbreviated to DPMDS. This compound is marketed as a solution containing 21 per cent by weight of DPMDS, which corresponds to 10 per cent mercury on a metallic basis.

Mercury vapor was detected physically, chemically, and biologically. The most reliable method involved the use of the Vapor Detector manufactured by the General Electric Company. This instrument depends upon the strong absorption by mercury vapor of ultraviolet radiation of wavelength 2537 A. It contains a low-pressure mercury-vapor lamp as a source of radiation, a chamber through which the air being sampled is passed by means of a built-in blower, and a photocell that is connected to an ammeter through a bridge circuit. In use, the higher the deflection of the instrument, the more mercury vapor is present. With a calibrated instrument, mercury vapor can be detected quantitatively and readily in concentrations ranging from 0.01 to 2.4 mg. of mercury vapor per cubic meter of air. A calibrated Vapor Detector was used extensively in the present investigation.

The Vapor Detector measures the concentration of mercury vapor in a sample of air at a given time. In the present studies, measurements were made to provide an estimate of the rate of vaporization of mercury from paint films, rather than the total amount of mercury liberated. Inasmuch as mercury was volatilized slowly from paint films, the painted surface was sealed in a screw-top test tube and held for a period to permit accumulation of a measureable amount of mercury vapor. To determine differences between treatments, moderate instrument deflections are necessary.

Preliminary measurements were therefore made to assure that incubation of paint films in sealed tubes for a period as long as 19 hours still gave an estimate of the rate of mercury liberation, rather than the amount liberated at or near the equilibrium state. A number of sheets of filter paper were coated with the standard mercury paint, allowed to dry for a day, and then sealed in tubes for 19 hours. Then Vapor Detector readings were made on the air in these tubes. Because varying amounts of paint were applied to the papers, the meter readings (arbitrary units) ranged from 29 to 69. The paint-coated papers were then transferred to clean tubes, sealed for 30 minutes and read again. These readings ranged from 10 to 20. The ratios of the 30-minute readings to the 19-hour readings were reasonably constant, ranging from 0.23 to 0.34. The magnitude of this ratio was not related to the magnitude of the instrument reading. These data indicate that in a 19-hour incubation period, the system has not approached equilibrium. Under these conditions, the mean concentration of mercury vapor in the atmosphere of the tube is a measure of the rate of liberation of mercury vapor into the atmosphere and not of the saturation vapor pressure.

An experiment tested whether the response of the Vapor Detector was proportional to the area of dried standard mercury paint exposed. The standard mercury paint was applied with a brush to large sheets of filter paper and allowed to dry. Then seven replicate sheets were cut from this for each of the following areas: 1, 2, 4, 8, 16, and 32 square centimeters. The 42 samples with corresponding controls were then sealed for 19 hours in screw-top tubes and the resulting concentrations of mercury vapor were determined with the Vapor Detector. Averages of the seven replicates for each area are reported in Table 1. Paint

films of the standard control paint treated in the same manner caused no deflection of the Vapor Detector. Therefore deflections with the standard mercury paint were caused by mercury vapor or by volatile mercury compounds which absorb ultraviolet radiation of wavelength 2537 A. Evidently the Vapor Detector quantitatively measures the amount of mercury vapor released under the conditions of use described.

Table 1. **Relation of area of mercury paint coating to concentration of mercury vapor released**

Area of coating	Concentration of mercury vapor
Square centimeters	*Milligrams per cubic meter*
0	0.00
1	0.02
2	0.05
4	0.09
8	0.23
16	0.35
32	0.66

Three biological assays were used to detect mercury vapor or volatile mercury compounds. In the course of this investigation mercury vapor was found to prevent the abscission of Pinto bean leaves. This response is quantitative in the range from 0.06 to 0.9 mg. of mercury per cubic meter of air. Details of this assay are reported elsewhere (Dimond & Waggoner, 1955). Trifoliate leaves are removed from plants and two test objects are prepared from each leaf. One consists of a 1 cm. length of the petiole with stubs of the lateral petiolelets and the other of a 1 cm. length of the central petiolelet with the base of the leaflet above the stipule. These are incubated in Petri dishes on a water agar suface. In the presence of mercury vapor no abscission occurs whereas control material abscinds in 4 days. When many test objects are sealed in a Petri dish with a source of mercury vapor, the proportion of abscissions occurring out of the total number possible is related to the concentration of mercury vapor. This response has been calibrated against that of a Vapor Detector (Dimond & Waggoner, 1955).

Because Better Times roses readily show mercury injury, cut flowers were confined in plastic containers with dried paint films. The response of roses was variable and served only as a qualitative test for the presence of mercury. Mercury vapor caused an early dropping of petals and sometimes caused the petals to become either pale pink or purple in color. In tests, the severity of response was graded on a scale from 0 (no effect) to 4 (rapid and complete dropping of petals).

Broad bean plants were reported by Zimmerman & Crocker (1934) as being very sensitive to mercury. Their value in assays for mercury vapor was accordingly examined. Leaves were removed from seedlings and their petioles wrapped in wet cotton and placed in shell vials full of water. When these were sealed in 1½- x 10-inch test tubes containing a source of mercury vapor such as a paint coating, mercury injury

appeared in from 1 to 4 days. The response is not limited to mercury and the assay is useful only when controls indicate that no interfering substances are present. Injury was graded on a scale from 0 to 4, the latter grade designating completely blackened leaves.

Toxicity of mercury-containing paint to roses

Three observations indicated that paints containing DPMDS are toxic to certain varieties of roses. In the first place, a standard paint formulation containing no mercury had been marketed by one manufacturer for greenhouse use in this area for a number of years and had not caused injury; when DPMDS was added to this formulation, rose growers using it noted injury but only on susceptible rose varieties. Butterfield (1954) has reported a test in which a house planted to Briarcliff roses was coated August 30, 1954 with a DPMDS-containing paint. On September 18 typical injury on these roses was first noted and it had become severe by September 24, 1954.

The experience of a Connecticut grower verifies these observations. Of two adjacent houses in one range, both of which contained Better Times roses, one was painted and the other was not. The sashbars and metal parts of one half of one house were coated with a paint containing 0.525 per cent DPMDS in July 1954. During the summer no injury developed. From September on, cool nights required that ventilators be closed and symptoms typical of mercury injury developed on all Better Times roses in this house. These plants had to be discarded by the end of 1954 because of the injury. In the unpainted house the flowers remained normal in color and production during the period from July 1954 to May 1955.

Cause of the injury to roses

That mercury vapor or volatile mercury compounds escape from the paint and cause the injury to roses is indicated by a number of characteristics of the problem. The symptoms on susceptible rose varieties exposed to paint containing DPMDS are identical with those described on Briarcliff roses when exposed to mercury vapor, arising from mercury compounds (Zimmerman & Crocker, 1934). No other known volatile compound affects roses in this way. In addition, only varieties of roses known to be susceptible to mercury injury are affected by mercury-containing paints.

More mercury was detected in leaves and petals of injured Better Times rose plants grown in a greenhouse that was painted with a DPMDS-containing paint than in normal plants not exposed to this paint. Thus, analyses for mercury were made on each type of plant. The normal plants were taken from a house to which no mercury paint had been applied. The injured plants were of the same variety and came from the adjacent house in the same range, half of which had been coated with a DPMDS-containing paint 5 months earlier. Analyses revealed 1.3 parts per million of mercury in petals from injured flowers, but only 0.2 parts per million in normal ones. Injured leaves contained

3.3 parts per million of mercury as compared with 0.07 parts per million in normal leaves. The above figures are on a fresh-weight basis. Large amounts of mercury were still present in the 5-month-old dried paint film.

The mercury in injured plants continues to affect flower color after plants are removed from an environment containing mercury vapor. Evidently, too, the mercury in vegetative parts of such plants is translocated to new flower buds as they develop. Thus, an injured plant free of soil was brought to the greenhouse at The Connecticut Agricultural Experiment Station, and planted in sand Three months after transplanting the plant produced new flowers that showed typical mercury injury, the petals ranging in color from white through pale pink to the intense red characteristic of the Better Times rose (Figure 1). Petals from such injured flowers contained 0.6 parts per million of mercury on a fresh weight basis as compared with 0.2 parts per million in normal flowers from plants not exposed to mercury.

Apparently mercury is also taken by the plant from the soil. Zimmerman and Crocker demonstrated the decomposition of mercury compounds in soils high in organic matter and detected mercury in leaves of plants grown in soils to which mercuric chloride was added (1934).

A rose grower who painted his greenhouse in 1954 noted injury on his plants in the fall when ventilators remained closed. He purchased new plants and placed some of them in the same greenhouse in old soil, while planting others in fresh soil. Old plants showing injury, were also divided in two lots, one lot remaining in old soil and the others being transplanted to fresh soil. Old plants in old soil showed maximum injury. Old plants in new soil partially outgrew the injury but were stunted and low in production. New plants in old soil grew more rapidly but were lower in production than they should have been. New plants in new soil showed but slight injury. Old plants in new soil might have been expected to continue to show some injury because of the mercury already contained in leaves and other vegetative parts of the plant. New plants in old soil apparently absorbed some mercury from the soil, as indicated by their lower rate of growth and reduced flower production.

The foregoing evidence suggests that DPMDS-containing paints release either mercury vapor or volatile mercury compounds which cause the injury to roses. Experiments were undertaken to determine whether mercury vapor is the volatile product arising from DPMDS. To test for mercury vapor arising from DPMDS a specific method for detecting mercury vapor was used, following the procedure of Zimmerman & Crocker (1934). This method is based on the high affinity of gold foil for mercury vapor with which it forms an amalgam. Gold foil is placed in a sealed tube with the source of the mercury vapor and incubated for several hours. At the end of this time, the gold foil is removed to a small test tube and the neck of the tube is drawn to a capillary that serves as an air condenser. Then the gold foil in the bottom of the tube is strongly heated, driving off as vapor any mercury dissolved in

FIGURE 1. Mercury injury to Better Times rose arising 3 months after plant was removed from environment containing mercury vapor. The soil was removed and the plant repotted in fresh sand on removal from the greenhouse coated with paint containing DPMDS.

the gold. This mercury condenses on the neck of the capillary. The top portion of the tube, containing the condensed mercury, is cut off and sealed in a screw-top test tube containing iodine crystals. Any mercury in the capillary reacts with iodine vapor to form a brick-red deposit of mercuric iodide that is readily visible even when the amount of condensed mercury is so small as not to be visible before the reaction.

To perform this experiment, filter paper circles 9 cm. in diameter were coated separately with the following materials: The standard mercury paint, DPMDS alone, enamel grinding oil alone (an oil in which

pigments are ground prior to formulation of paints), and a mixture of enamel grinding oil and DPMDS. Untreated paper served as a control. These papers were sealed in screw-top test tubes under the caps of which was fastened a sheet of gold foil. As a standard source of mercury, another series of tubes was used containing metallic mercury together with the gold foil. In addition one complete series of tubes was set up for analysis by the Vapor Detector. After incubation for 3 days, chemical tests were completed (Table 2). All of these results were confirmed in an independent experiment.

Table 2. **Release of mercury vapor from mercury, DPMDS, and combinations of DPMDS with paint**

Test material	HgI_2 method*	Vapor Detector
		Milligrams per cubic meter
Check	0	0.00
Enamel grinding oil	0	0.00
DPMDS	1	0.66
Standard mercury paint	2	1.56
DPMDS plus enamel grinding oil	3.5	2.42
Metallic mercury	3.5	2.30

*Responses ranked in increasing order of intensity, no response being indicated as 0.

The mercuric iodide method is specific for mercury vapor and will not respond to volatile phenyl mercury compounds. The correspondence between results of the mercuric iodide method and those obtained with the Vapor Detector indicates that mercury vapor is the volatile material to which the Vapor Detector is responding. Crocker and Zimmerman (1934) have already demonstrated the toxicity of mercury vapor to a number of plants. Evidently DPMDS decomposes slowly, forming metallic mercury. In paints the release of mercury vapor from DPMDS is more rapid than when DPMDS alone is present. Certain components in paints apparently hasten the decomposition of DPMDS materially.

Vaporization of mercury occurs much more rapidly than of DPMDS, as can be seen from a comparison of the vapor pressures of these two materials. Thus DPMDS in crystalline form volatilizes to the extent of 1.97 mg. per cubic meter of air at 40° C. in a confined space. This corresponds to 0.95×10^{-3} mg. of mercury on a metallic basis per liter of air. Mercury itself at this same temperature has a vapor pressure of 6.08×10^{-2} mm. of mercury which is equivalent to 47.5 mg. of mercury per liter of air under the same circumstances. Thus metallic mercury is roughly 50,000 times as volatile as DPMDS. At the temperatures prevailing in a greenhouse, the vapor pressure of mercury would also be much higher than for DPMDS. Thus any material which effects a breakdown of only a small proportion of the DPMDS to metallic mercury will result in a considerable increase in the amount of mercury released from the paint film.

Effect of paint components on decomposition of DPMDS

As has been shown, the Vapor Detector was used in these studies so as to measure the rate of release of mercury vapor on decomposition of DPMDS. Accordingly a rapid means is at hand for determining the effect of paint components on the decomposition of DPMDS. To study this, various components were employed alone or when mixed with an equal volume of DPMDS as formulated for sale. Materials were applied with a brush to 9 cm. filter paper circles and allowed to dry for 2 days. Then the coated papers were sealed for 19 hours in screw-top test tubes to permit mercury vapor to be released in readily detectable concentrations. Finally the atmosphere in these tubes was sampled and the mercury vapor concentration determined with the Vapor Detector.

None of the papers coated with formulants alone caused any deflection of the Vapor Detector. With mixtures of DPMDS and single formulants of paint, however, the concentration of mercury vapor in all but two combinations was higher than when DPMDS alone was used (Table 3). Outstanding in this regard were mixtures of DPMDS with Rheotol, Araplaz, or enamel grinding oil, two of which resulted in the maximum significant instrument deflection due to mercury vapor.

Table 3. **The effect of components in a greenhouse white paint on the liberation of mercury vapor from DPMDS**

Combination	Mercury vapor liberated
	Mg. per cubic meter of air
DPMDS alone	0.66
Rheotol plus DPMDS	1.89
Anti-skinning agent plus DPMDS	0.38
Pb naphthenate dried plus DPMDS	1.14
Mn naphthenate dried plus DPMDS	1.23
Co naphthenate dried plus DPMDS	0.96
Araplaz plus DPMDS	2.42
Enamel grinding oil plus DPMDS	2.42
Mineral spirits A plus DPMDS	1.23
Mineral spirits B plus DPMDS	0.24

Even though one paint contains no mercury, components may influence the behavior of a mercury-containing paint film if the two are applied in the same greenhouse. This was suggested by the experience of one Connecticut grower in the summer of 1954. He painted the sashbars of eight houses in a single range with a white paint containing 0.84 per cent DPMDS. The metal beams of these houses were rusted and were coated with aluminum paint containing no mercury. Two formulations of aluminum paint were used in this operation. In seven of the houses the metal was coated with ordinary aluminum paint. No mercury injury appeared on Better Times roses in these houses. In one house corrosion-resistant aluminum paint was applied. In the fall of

1954 Better Times roses in this single house developed symptoms of mercury injury, several weeks after the paint was applied. All eight houses were similar in exposure to sunlight and were watered and maintained at similar temperatures. Such experience suggests that components of one paint may affect the release of mercury vapor from another paint containing DPMDS.

An experiment was set up to test this possibility and to confirm the effect of enamel grinding oil on DPMDS. Materials were dropped on filter paper from a standard pipette, thus better controlling the amount of material applied than when they were applied with a brush. One drop of formulated DPMDS from the standard pipette weighed 15.3 mg. which corresponds to 3.2 mg. pure DPMDS. Five replicates of each treatment were prepared. When mixtures were involved, they were applied to the paper separately but in contact with each other. The design of the experiment is evident from Table 4. Treated papers were allowed to stand for a day, and then were sealed in screw-top test tubes. The mercury vapor concentration in the atmosphere of these tubes was then measured with the Vapor Detector. Values reported in Table 4 are means of the five replicate treatments. These data indicate that components in either aluminum or white paints accelerate the decomposition of DPMDS as measured by the increased release of mercury vapor that they cause.

Table 4. **The effect of enamel grinding oil and aluminum paint on the liberation of mercury from DPMDS**

Drops of DPMDS	DPMDS alone	8 drops enamel grinding oil	8 drops aluminum paint
	Milligrams of mercury vapor per cubic meter of air		
0	0.00	0.00	0.00
1	0.28	1.88	0.86
2	0.32	2.00	1.20
4	0.26	2.10	1.40
8	0.76	2.10	1.90

The components in one formulation of aluminum paint were tested in a similar manner. In this experiment 4 drops of the formulant were applied to each of 4 filter paper circles. The aluminum paste was spread on the paper with a spatula. One series of filter papers containing each formulant singly was not treated further. The second, third, and fourth series respectively received 1, 2, or 4 drops of DPMDS so that it was in contact with the deposit of formulant. After the papers dried in air for 1 day and were incubated in sealed tubes overnight, the mercury vapor concentration in the tubes was determined with the Vapor Detector (Table 5). Of the materials examined, dipentene, aluminum paste, and enamel grinding oil definitely increased the liberation of mercury vapor from DPMDS. Calcium naphthenate may have caused a slight increase.

Table 5. **Effect of some formulants of aluminum paints on the release of volatile mercury from DPMDS**

Formulant	no. drops DPMDS added			
	0	1	2	4
	Milligrams of mercury per cubic meter of air			
Calcium naphthenate	0.00	0.36	0.67	0.50
Cobalt naphthenate	0.00	0.14	0.58	0.98
Lead naphthenate	0.00	0.11	0.50	0.41
Dipentene	0.00	0.50	0.41	1.34
Aluminum paste	0.00	0.19	1.34	1.90
Bakelite resin #4036*	0.00	0.006	0.36	0.00
Bakelite resin #XP254*	0.00	0.27	0.25	0.86
Enamel grinding oil	0.00	0.74	1.38	1.60
Acetone	0.00	0.009	0.14	1.29
Nothing	0.00	0.18	0.18	0.71

*10 per cent solution in acetone.

Age of paint films in relation to release of mercury vapor

For the grower who has already applied a paint containing DPMDS in his greenhouse, it becomes important to know how long mercury vapor will continue to be released if no corrective treatments are applied. To examine this matter, filter paper circles were coated with the standard mercury paint and exposed in a greenhouse for various times. At the end of these periods they were confined in sealed tubes overnight and the rate of release of mercury vapor was determined with the Vapor Detector. In this experiment duplicate paint films 1, 2, 3, 4, 5, 8, 9, 11, 12, 14, 16, 20, and 24 days old were examined. Averaged results for paint films of given ages indicated no decrease whatsoever with time in rate of release of mercury vapor. Thus, a 24-day-old paint film liberated 1.09 mg. of mercury vapor per $m.^3$ in 19 hours and a 1-day-old paint film liberated 0.88 mg. of mercury per $m.^3$ of air in the same time. These data suggest that mercury vapor will continue to be released for a long time. Because one Connecticut grower painted his houses in July and did not observe injury on roses until fall when ventilators were kept closed, it would seem that liberation of mercury will continue unabated over several months.

Treatments to reduce the liberation of mercury from paint films

Release of mercury vapor from dried paint films containing DPMDS apparently does not abate within any short period of time. Therefore, the grower who has applied such paint to his greenhouse may need a means of halting mercury release so that the house can be used for rose growing.

Experiments were undertaken to test a number of materials as mercury vapor barriers. Both physical and chemical barriers were used. The chemical barriers contained materials that might react with mercury vapor as it arises from the paint film. If a stable product were formed, there might be little mercury lost from the painted surface.

In the first experiment a number of coatings were tested as physical barriers. In addition one chemical barrier containing lime sulfur (calcium polysulfide) was tested. Calcium polysulfide was used because polysulfides react with mercury and also because this compound, when moist, slowly releases hydrogen sulfide which also reacts with mercury to form mercuric sulfide, a very stable compound. A formulation that would spread evenly over a painted surface was prepared by mixing into a paste 5 parts by weight of dry lime sulfur, 10 parts of wheat wallpaper size, and 100 parts of water.

Filter paper circles were painted with the standard mercury paint on both sides and allowed to dry for 4 days. Then the several coatings under test as mercury vapor barriers were applied over the paint film and allowed to dry 4 days. As controls the several overcoating materials were applied to both sides of fresh filter papers. Five replicates were prepared for each treatment. In the usual manner the release of mercury vapor through the barrier coating was determined after 19 hours in a sealed tube with the Vapor Detector.

None of the materials under test as mercury vapor barriers caused any deflection of the Vapor Detector when applied alone. However, all of these materials except the lime sulfur paste were wholly ineffective as mercury vapor barriers (Table 6). The lime sulfur coating was highly effective.

Table 6. **Effectiveness as mercury vapor barriers of coatings applied over the standard mercury paint film**

Coating	Quantity of mercury vapor passing the coating
	Mg. of mercury per m.^{3}
Dow Corning Silicone #803	1.94
Dow Corning Silicone #1107	1.80
Polyethylene nonporous white primer	1.92
Alkyd resin paint	1.32
Chlorinated rubber base paint	0.97
Lime sulfur paste	0.003
Standard mercury paint only	2.00
Standard control paint only	0.00

Another series of experiments tested the effectiveness of a white paint in preventing the escape of mercury vapor. Also a number of chemical barriers were evaluated. All of the chemical barriers were prepared in a wheat flour paste at a concentration of 5 per cent by weight. In some tests 8-quinolinol was formulated as a paste and in others a paint containing 8-quinolinol was used. This compound binds some metals quite firmly and was tested to determine whether its affinity for mercury made it useful in the present problem. Wettable sulfur was used in a wheat paste because it might also bind mercury vapor. Also the lime sulfur paste was retested.

Calcium chloride in wheat paste was tested as a possible chemical barrier because the phenyl mercury radical, which behaves chemically like silver ion in many reactions, might form insoluble phenyl mercury chloride. If formed and stable, phenyl mercury chloride would not release mercury vapor.

In this series of tests the standard mercury paint was applied to one surface of filter paper circles, allowed to dry for 1 day and then the coating under test was applied over the painted surface. Also the coating under test was applied directly to another series of filter paper circles. All of these were used in a series of biological tests and in tests involving the Vapor Detector. In each separate test, freshly coated surfaces were used. All coatings were allowed to dry for 1 day before being tested either with the Vapor Detector or in a biological assay.

When confined with freshly picked Better Times rose buds, the mercury-containing paint caused moderate petal abscission but the same paint without mercury caused none. Damp-proof white paint, 8-quinolinol paint, and calcium chloride paste did not reduce mercury injury whereas the sulfur and lime sulfur paste apparently prevented injury effectively.

In the broad bean test the standard mercury paint caused moderate injury but the standard control paint caused none. The damp-proof white paint caused barely perceptible injury by itself. No mercury injury developed when damp-proof white paint was applied as a coating over the standard mercury paint. Lime sulfur paste caused no injury by itself and prevented mercury injury when applied over the standard mercury paint. Calcium chloride paste and 8-quinolinol paint or paste were ineffective as coatings over the standard mercury paint. The injury produced by application of damp-proof aluminum paint over the standard mercury paint was equal to that caused by metallic mercury.

Responses of these barriers alone and when applied over the standard mercury paint were further tested in the bean abscission assay and

Table 7. **Effect of coatings as mercury vapor barriers**

Coating under test	Conc. mercury vapor passed through barrier coating over standard mercury paint	Abscission in bean test*	
		Coating alone	Coating over standard mercury paint
	Mg. Hg. per m^3	*Per cent*	*Per cent*
Standard mercury paint only	1.56		0
Standard control paint only	0.00	50	
White paint	2.30	67	0
Aluminum paint	0.90	84	25
Sulfur paste	0.41	100	0
Lime sulfur paste	0.00	92	84
$CaCl_2$ paste	0.27	100	0
8-quinolinol paste or paint	0.52	0	0
Metallic mercury	2.30		0
No treatment	0.00	100	

*Mercury vapor prevents the natural abscission of bean petioles.

by means of the vapor detector (Table 7). With the exception of the paint containing 8-quinolinol, none of the materials under test affected the Vapor Detector when applied as a coating directly to the filter paper.

Evidently the white paint is partially effective as a mercury vapor barrier but is probably not sufficiently so to prevent plant injury. Over the standard mercury paint, aluminum paint caused more rapid liberation of mercury vapor than did the standard mercury paint alone. Sulfur paste is partially but probably not practically effective: sufficient mercury vapor is released to prevent abscission in the bean assay. The same is true of the calcium chloride paste. Interference of 8-quinolinol with mercury in the bean assay and the Vapor Detector test makes an evaluation of this treatment difficult. However, its injuriousness to cut roses suggests it may not be a practical treatment in any case. Lime sulfur paste was the only effective treatment by all criteria. Its behavior in the first experiment is therefore confirmed.

Further experiments measured the effectiveness of lime sulfur paste as a coating over the standard mercury paint in humid and dry air. The standard mercury paint was applied to one side of a number of filter paper circles, and allowed to dry for 1 day. To half of these, lime sulfur paste was applied over the painted surface. Samples of each of these two lots were then sealed in dry screw-top test tubes whereas the rest were sealed in tubes in a saturated atmosphere. After these samples had incubated in tubes for 5 days, the atmosphere in the tubes was examined with the Vapor Detector. Table 8 reports the averages of duplicate measurements for each of the four treatments. Apparently somewhat less mercury vapor is released from the standard mercury paint film in saturated than in dry air. As would be expected, the lime sulfur coating provides a more effective barrier to mercury vapor in a humid than in a dry atmosphere.

Table 8. **Effect of moisture on the release of mercury vapor from the standard mercury paint and on lime sulfur paste as a mercury vapor barrier**

Incubation	No lime sulfur	Lime sulfur coating
	Milligrams of mercury per cubic meter of air	
Dry air	1.64	0.29
Saturated air	0.88	0.06

The length of time that lime sulfur paste provides an effective mercury barrier was examined. Filter paper circles were painted on one side only with the standard mercury paint 16 days prior to being read with the Vapor Detector. On days 15, 11, 7, 5, 3, 2, and 1 prior to being read, lime sulfur paste was applied over the painted surface. Four sheets of paper were coated on each day. Two sheets in each lot were held in a greenhouse. This is the humidity of actual use. Two others were held in the laboratory. All of the samples were sealed in screw-top test tubes 18 hours before being read during which time they were held in a saturated or dry atmosphere according to whether they had been held in the greenhouse or laboratory air during their aging

period. Vapor Detector readings on the 16th day were averaged for the duplicates and are reported in Table 9.

Table 9. **Relation of age of lime sulfur coating and humidity on its effectiveness as a mercury vapor barrier**

Age of lime sulfur coating	Mercury escaping through coating per cubic meter of air	
	Humid air	Dry air
Days	*Mg. of mercury*	*Mg. of mercury*
15	0.003	0.002
11	0.005	0.004
7	0.005	0.005
5	0.004	0.005
3	0.003	0.006
2	0.004	0.003
1	0.002	0.003
Lime sulfur check (no Hg)	0.000	
Standard Hg paint	1.09	

The quantities of mercury vapor escaping through the lime sulfur coating were negligible under all conditions. Evidently sufficient moisture was present in laboratory air to activate the lime sulfur coating as a mercury vapor barrier. There was no evidence within 15 days of any loss in effectiveness of the lime sulfur coating.

The value of the lime sulfur coating was tested in a commercial greenhouse that had been painted with a mercury-containing paint. In January, 1955 lime sulfur paste was applied to all surfaces that had received the mercury-containing paint in July, 1954. Better Times rose flowers, produced in an adjacent house and not previously exposed to mercury vapor, were brought as bouquets into the treated house. Before receiving the lime sulfur treatment, such bouquets had turned blue and shown premature petal dropping. After the house was treated, such bouquets remained normal. Early in January, 1955 all injured rose plants were removed from the treated house, the benches replaced and new soil was brought in. New Better Times rose plants were planted in one bench of this house. These plants grew normally and produced a crop for Easter, 1955. To date (May, 1955) no symptoms of mercury injury have developed in these plants.

The possibility was examined that the rapid vaporization of mercury from paint films following the application of certain aluminum paints would lead to a depletion of mercury in the underlying coat of paint within a short time. To test this, the standard mercury paint was applied to one surface of duplicate filter paper circles 16, 12, 8, 6, 4, 3, and 2 days before being read. On the day following the first application of paint, each sheet received a film of aluminum paint. The coated papers were hung in the greenhouse and on the day before readings were to be made, they were sealed in tubes for 19 hours. Then the air in the tubes was analyzed for mercury vapor with the Vapor

Detector. Averaged readings for the duplicates are presented in Table 10. Contrary to expectation, the older the coating the more mercury vapor was liberated. This behavior probably resulted from the slowness of the migration into the mercury-containing paint film of a material in the aluminum paint that hastens the decomposition of DPMDS. There was no evidence within the interval covered by this experiment of any decrease in rate of release of mercury vapor with time. The amount of mercury escaping within the 16-day period was very small as compared with that remaining in the film. Therefore, one would expect release of mercury vapor to continue over many weeks.

Table 10. **Effect of time on the amount of mercury vapor released from paint films overcoated with aluminum paint**

Age of aluminum paint film	Mercury escaping through aluminum paint film
Days	*Milligrams*
16	2.06
12	1.50
8	0.86
6	1.23
4	1.14
3	1.23
2	1.08
Aluminum paint only, no mercury	0.00

Discussion

The release of mercury vapor from DPMDS-containing paint films is readily measured with the Vapor Detector only if the paint film is sealed in a small container until the concentration rises to a readily detectable level. Sampling the air over a 1-day-old painted surface in an open room results either in no response of the Vapor Detector or in the minimum detectable response. Butterfield (1954) has reported that only a slight deflection in the instrument was obtained when it sampled air immediately over the painted surface the day following application of DPMDS-containing paint in a greenhouse at the Waltham Field Station. The data on which this report is based are that the instrument showed a deflection corresponding to from 0.01 to 0.02 mg. of mercury per cubic meter of air when held directly over the painted surface. However, the Vapor Detector gave a deflection corresponding to 1.2 mg. of mercury per cubic meter of air when held over the surface of a freshly opened bucket of paint containing DPMDS. This paint was identical with the standard mercury paint used in the present studies. The instrument showed no deflection when held over a freshly opened bucket of paint identical with the standard control paint. The Vapor Detector would probably fail to give a deflection when sampling greenhouse air away from a surface that was freshly coated with DPMDS-containing paint. If so, the concentration of mer-

cury vapor in the air is too low to measure with the Vapor Detector and would be less than 0.01 mg. of mercury per cubic meter of air.

In spite of this, susceptible rose plants become injured by continued exposure to mercury vapor at concentrations of 0.01 mg. per cubic meter or less. This concentration corresponds to 0.0083 parts per million of air or less on a weight basis (dry air at 68° F., 760 mm. pressure). Analyses of injured as compared with normal rose plants have shown that exposed plants absorb mercury under these conditions. Injured leaves have been found to contain as much as 3.3 parts per million of mercury on a fresh weight basis. Comparison of the concentration of mercury vapor in air with that in the leaf readily shows that the plant has accumulated mercury at levels above that of the air during exposure. Levels of mercury in flowers are similarly higher than occur in the air. Whether the petals absorb the mercury directly or it arrives there through translocation from leaves has not been determined. However, it has been shown that mercury is translocated from leaves to developing buds by removing injured plants from the environment and detecting higher than normal amounts of mercury in the petals of flowers which subsequently develop.

These findings have implications when food crops are grown in greenhouses. When mercury levels become sufficiently high in leaves of susceptible plants, they become injured. Probably mercury absorption occurs when plants are exposed to mercury vapor even when the plants are not susceptible to injury. Tomatoes and a number of other plants grown in greenhouses have been shown by Zimmerman & Crocker (1934) to absorb measureable amounts of mercury in leaves when exposed to mercury vapor. In view of the demonstrated translocation of mercury from leaves to other parts of the plant, one may expect the edible portions of food crops, grown in an environment containing mercury vapor, to contain measureable amounts of mercury. Tomato fruits grown in a greenhouse where mercury vapor is present may well contain mercury. Under the Food, Drug, and Cosmetic Act, no mercury is tolerated on or in foods.

Summary

Better Times, Briarcliff, and related varieties of roses are injured by mercury vapor. Such roses grown in greenhouses have shown severe injury when the sashbars of houses have been coated with paints containing di-(phenylmercuric)dodecenyl succinate (DPMDS). The injury results from decomposition of DPMDS to mercury which is then released from the paint film as mercury vapor. Decomposition of DPMDS is hastened by a number of components in paints. Moreover, one paint, not containing mercury, may contain components that accelerate the liberation of mercury vapor from another paint containing DPMDS. Therefore, a stable formulation of paint containing DPMDS may still be a hazard to plants when another paint is applied in the same confined space. Mercury continues to be released from DPMDS-containing paints for a long time after it has been applied. There was no evidence of any decrease in rate of release of mercury vapor within a

24-day test period. Rose growers who painted their houses in July suffered no injury to roses for the first 3 months while the houses were open, but injury became severe from September on when ventilators were closed for periods during cool weather.

Mercury is accumulated by susceptible plants exposed to mercury vapor. Under some circumstances, it is translocated in the plant from vegetative portions to flowers. When food crops are involved, mercury may be present in the fruit, even when plants are not susceptible to mercury injury.

The greenhouse operator who has applied a DPMDS-containing paint in a greenhouse can reduce the liberation of mercury vapor from the paint film by applying 5 parts of dry lime sulfur, formulated in a paste consisting of 10 parts of wheat flour and 100 parts of water, over the DPMDS-containing paint film. When such treatment is applied with a brush to the painted surface, release of mercury vapor is almost completely eliminated for a considerable period of time. Controlled experiments indicated no loss in effectiveness of this coating within a 15-day period. In a commercial greenhouse, a single application of lime sulfur paste has been effective for the 5 months which have elapsed since it was applied.

Once rose plants show injury, they may produce unmarketable flowers for a considerable period, even if they are removed from an environment containing mercury vapor. There is some evidence, too, that mercury enters the plant through the soil. Under these conditions, replacement of soil and injured plants is indicated as a corrective measure.

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